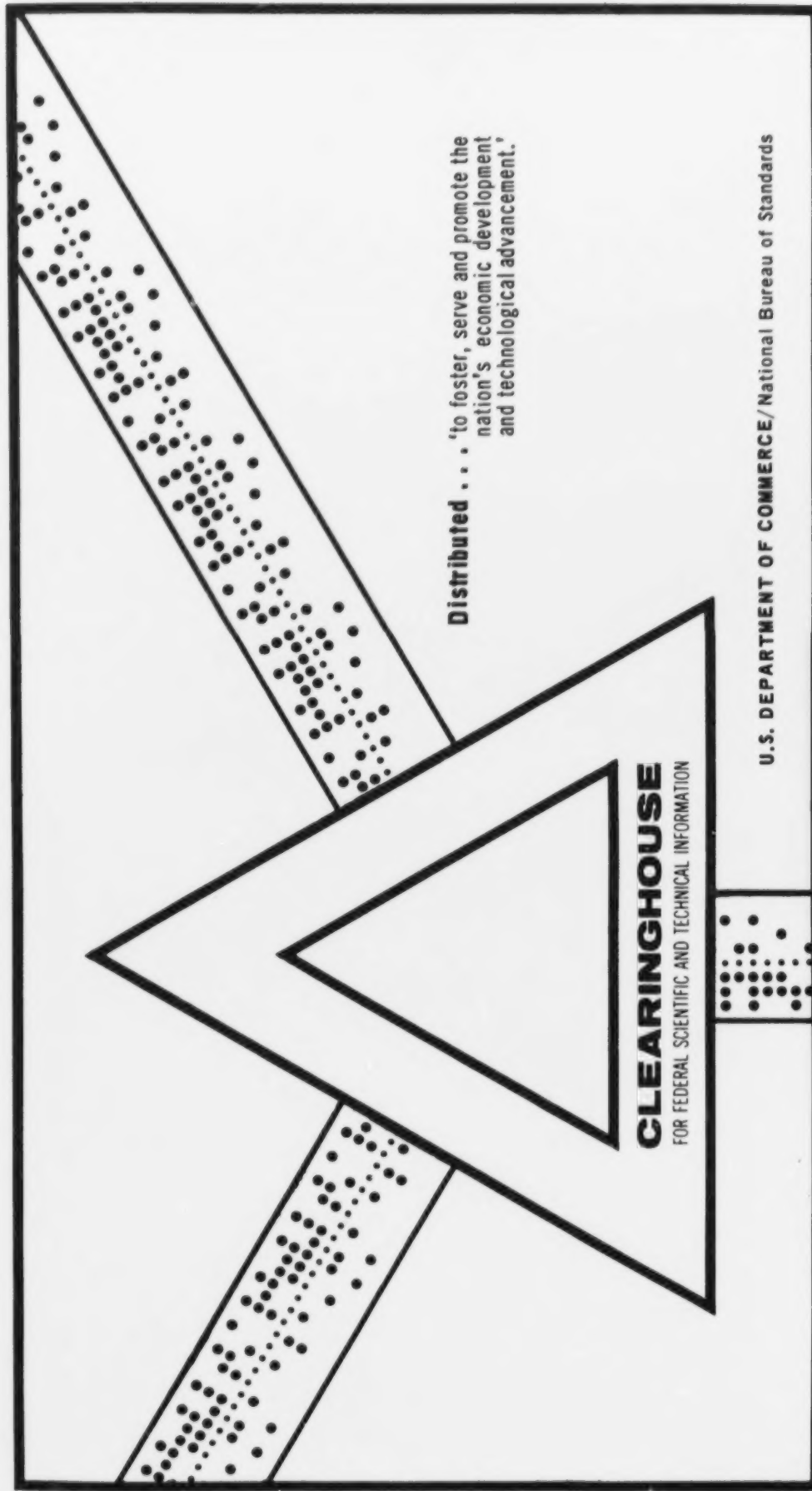


OIL DISPERSING CHEMICALS. A STUDY OF THE COMPOSITION, PROPERTIES
AND USE OF CHEMICALS FOR DISPERSING OIL SPILLS

Melvin Z. Poliakoff

Federal Water Pollution Control Administration
Edison, New Jersey

May 1969



U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

This document has been approved for public release and sale.

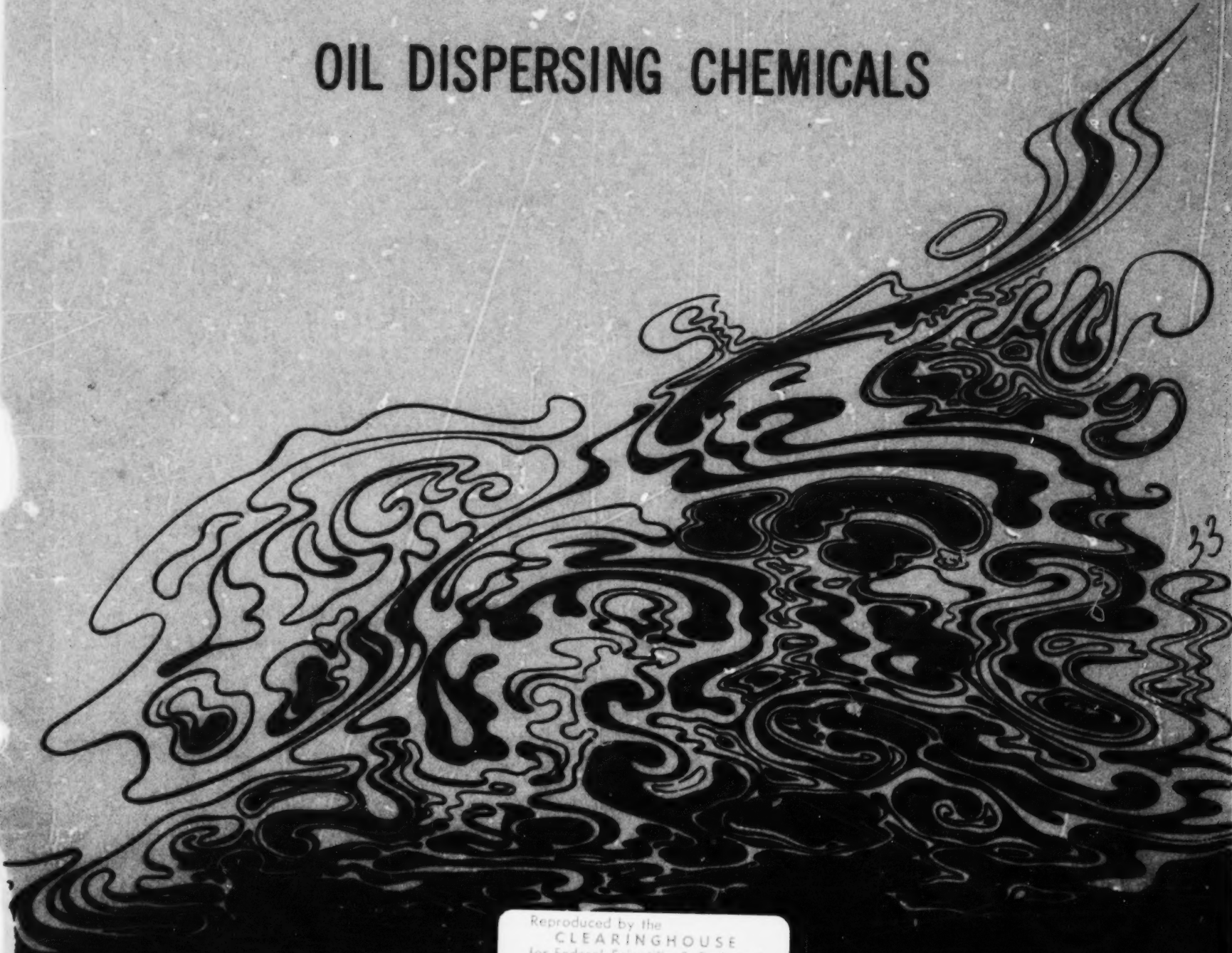


W70-0237 15080FHS05769
WATER POLLUTION CONTROL RESEARCH SERIES • ORD-1

W70-02037

PB188207

OIL DISPERSING CHEMICALS



Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va. 22151

DEPARTMENT OF THE INTERIOR • FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Reports describe the results and progress in the control and abatement of pollution of our Nation's waters. They provide a central source of information on the research, development and demonstration activities of the Federal Water Pollution Control Administration, Department of the Interior, through inhouse research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

Water Pollution Control Research Reports will be distributed to requesters as supplies permit. Requests should be sent to the Planning and Resources Office, Office of Research and Development, Federal Water Pollution Control Administration, Department of the Interior, Washington, D. C. 20242.

OIL DISPERSING CHEMICALS

A Study of the Composition, Properties and
Use of Chemicals for Dispersing Oil Spills

by

Melvin Z. Poliakoff

Consultant

Tenafly, New Jersey

for the

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

DEPARTMENT OF THE INTERIOR

Edison Water Quality Laboratory

Northeast Region

Edison, New Jersey, 08817

Program Number 15080FHS 05/69

Contract Number 14-12-549

DI-

May 1969

FWPCA Review Notice

This report has been reviewed by the Federal Water Pollution Control Administration and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Federal Water Pollution Control Administration, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

A "state-of-the-art" review is provided for chemicals which are used for dispersing spilled oil. Among the topics discussed are: the history of the development of oil spill dispersants; basic emulsion chemistry, including the nature and properties of surface active agents; chemical composition of oil spill dispersants, including a description of generic chemical types; production of dispersants, properties of dispersants; chemical analysis of oil spill dispersants; and the measurement of oil spill dispersing power.

KEY WORDS: Chemical analysis, chemicals, detergents, dispersion, emulsifiers, oil, surfactants, testing, water pollution control, emulsions.

TABLE OF CONTENTS

	Page
Conclusions -----	1
Introduction-----	2
Historical Development of Oil Spill Dispersants-----	3
Emulsion Chemistry-----	4
Surface active agents	
Emulsions	
Emulsion Stability	
Chemical Composition of Oil Spill Dispersants -----	8
Surfact active agents	
Solvents	
Other additives	
Production and Properties of Oil Spill-----	14
Dispersants	
Manufacture	
Relationship of physical properties to performance	
Chemical Analysis of Oil Spill Dispersants-----	16
Measuring Oil Spill Dispersing Power-----	19
A.S.T.M. tests	
Military specification tests	
Laboratory determination of dispersing potential	
Field testing	
References -----	26

CONCLUSIONS

The writer has attempted to provide an overview of the state-of-the-art of manufacturing and testing Oil Spill Dispersants.

The chemicals currently available for oil dispersant use were developed out of the existing body of knowledge of emulsion technology. Many of these materials have been used to "solve" emergency oil spill problems under a now badly outmoded concept of pollution control — which was to eliminate the immediate problem of visual pollution and fire hazard, with little or no prior evaluation of possible ecological consequences. This has led to considerable criticism of chemicals which sink, emulsify or disperse oil slicks (21). Improved methods of oil removal from the water, rather than dispersion in the water, are under development (22).

Nevertheless, the use of chemical dispersant methods may continue to find a place under closely controlled conditions where removal techniques are not practical. Such situations exist adjacent to and under docks and pilings, where the spill presents an immediate fire hazard, and where removal equipment is not readily available. Under these circumstances, the authorities in charge will weigh the possible ecological damage which chemical treatment might cause against the immediate hazards of no treatment. Reliable information concerning toxicity to marine life, as well as other effects of these chemicals, is essential before such evaluations can be made.

The promulgation of standardized toxicity test methods for oil dispersants will aid manufacturers in their own development of safer chemicals and methods of treating oil spills. Developments in this field will lead to products which are more effective at lower concentrations, less hazardous to handle, and more readily biodegradable, as well as less harmful to the ecology.

INTRODUCTION

This document was prepared by the author for the Federal Water Pollution Control Administration under Contract Number 14-12-549 in May 1969.

The objective was to furnish a state-of-the-art report on the composition, properties and uses of chemical dispersants used for treating oil spills on water. The work was specifically confined to chemical materials which function by virtue of their surface active, emulsifying, or dispersing properties.

The information furnished is based on literature search, as well as the experience and research of the author in this field.

HISTORICAL DEVELOPMENT OF OIL SPILL DISPERSANTS

In tracing the development of oil spill dispersants we need only go back as far as the early 1930's when water emulsifiable degreasers were in fairly widespread use. These degreasers were developed to answer the need for effective methods of cleaning oily and greasy surfaces. They possessed the properties of dissolving or dispersing in the grease or oil, and making the resultant mixture dispersible in water so that it could be flushed away with water.

The early products were composed mostly of soaps and solvents. The demands of the petroleum shipping industry required products that could be used effectively aboard ship with seawater. This led to the use of materials other than soaps as emulsifying agents because soap breaks down in seawater. Sulfonated petroleum oils and later more sophisticated synthetic detergents made their appearance in these products.

These emulsifying degreasers were widely used aboard ship for engine room maintenance, as well as for the clean out of petroleum cargo tanks prior to welding repairs and prior to upgrading of cargo.

Because of their effectiveness in cleanout of oil residues it was natural that they should be tried for treating oil spills. In some cases they were incorporated in oil slops prior to dumping overboard in order to minimize slick formation.

Considerable quantities of these degreasers are used by industry as well as by various governmental services. Some of the specifications describing water emulsifiable degreasers established by the various government units include the following:

P-C-576	Compound, grease cleaning, solvent emulsion
P-C-444	Cleaning compound, solvent soluble, grease emulsifying
MIL-C-7122	Compound, grease cleaning, solvent emulsion type
MIL-C-20207	Cleaning compound, solvent emulsion, grease removing
MIL-C-22230	Fuel Tank and bilge cleaner
MIL-C-22864	Solvent-emulsifier, oil slick
MIL-C-25179A	Compound, emulsion cleaning (for aircraft)

EMULSION CHEMISTRY

In any study of oil spill dispersants, familiarity with the surface active chemicals used, as well as the mechanisms of emulsion formation, is a necessary starting point. A brief review of these subjects will be helpful before examining the manufacture and performance of oil spill dispersants.

Surface Active Agents

Surface active agents are often defined according to their behavior in aqueous solutions (1). These solutions will usually wet surfaces readily, remove dirt, penetrate porous materials, disperse solid particles, emulsify oils and grease, and produce foam when stirred or shaken. All of these properties are interrelated, and no surface active agent possesses only one of them to the exclusion of the rest.

A compound may be called a wetting agent rather than a detergent because its wetting power is greater than its detergent power. Likewise a compound may be called an emulsifying agent rather than a detergent because its ability to emulsify oils is greater than its cleaning power.

The molecules of surface active agents are made up of two parts: a relatively large elongated part which is the hydrophobic portion, and a relatively small solubilizing polar group which is known as the hydrophylic portion. The antagonism of these two portions of the molecule and the balance between them gives the compound its surface active properties. When the proper balance between the two portions of the molecule exists, the substance neither dissolves completely nor remains completely undissolved, but rather concentrates at a liquid-liquid interface. In an emulsion, the molecules of surface active agent are so oriented that the hydrophylic groups are anchored in the aqueous phase and the hydrophobic groups project into the non-aqueous or oily phase.

Surface active agents are often divided into two broad classes depending on the character of their colloidal solutions in water. The first class, ionic surface active agents, form ions in solution, and like the soaps are typical colloidal electrolytes. The second class, the non-ionic surface active agents, do not ionize, but owe their solubility to the combined effect of a number of weak solubilizing groups such as ether linkages or hydroxy groups in the molecule.

A more detailed discussion of those surface active agents used in oil spill dispersants will be made in a later section on composition of these products.

Emulsions (2) (3)

A.S.T.M. (4) defines emulsion as "a suspension of fine particles or globules of one or more liquids in another liquid". The two liquids are of course mutually insoluble, and oil and water is our typical example. The stability of emulsions ranges from the "shake well before using" pharmaceutical preparations of a few years ago to such stable emulsions as homogenized milk. Surface active agents, emulsifying agents in particular, are used to stabilize the dispersion of the two insoluble liquids. The dispersed liquid is often called the internal or discontinuous phase, and the dispersing medium is called the external or continuous phase. Emulsions are often classified as to whether the oil is the dispersed phase — oil in water emulsions; or whether water is the dispersed phase — water in oil emulsions. The type of emulsion formed is a function of viscosity, dielectric constant, the concentration of ingredients, specific gravity and hydrophile-lipophile balance of the emulsifying agents.

Griffin (5) (6) has established helpful data on hydrophile-lipophile balance (HLB) of emulsifying agents as effecting emulsion formation and stability.

A hydrophylic emulsifying agent, one in which the hydrophylic portion of the molecule is large with respect to the hydrophobic portion, will tend to form oil in water emulsions. Hydrophobic emulsifying agents in which the hydrophobic portion of the molecule is large with respect to the hydrophylic portion of the molecule will tend to form water in oil emulsions. Water in oil emulsions can be recognized by the fact that they do not disperse in water. They will coalesce when placed on the surface of water. These may well have been the globs of "chocolate mousse" noted in some of the Torrey Canyon references (7).

As an aid in predicting emulsification tendencies of surface active agents, these compounds have been classified as to hydrophile-lipophile balance. The HLB of a surface active agent can be determined approximately by the appearance of its aqueous solutions. See Table I (3).

TABLE I
HLB DETERMINATION BY DISPERSIBILITY

<u>Appearance in Aqueous Solution</u>	<u>HLB Range</u>
No dispersibility	1 to 4
Poor dispersion	3 to 6
Milky dispersion after vigorous agitation	6 to 8
Stable milky dispersion	8 to 10
Translucent to clear dispersion	10 to 13
Clear solution	13+

The applications for various surface active agents can be predicted by the HLB. From the data in Table II (4) it will be noted that oil in water emulsifiers should preferably be selected with an HLB range above 8.

TABLE II
HLB RANGES AND THEIR APPLICATIONS

<u>Range</u>	<u>Application</u>
3 to 6	Water in oil emulsifier
7 to 9	Wetting agent
8 to 18	Oil in water emulsifier
13 to 15	Detergent
15 to 18	Solublizer

Becher (4) has pointed out that spreading phenomena, which are susceptible to direct observation, may be used as a rapid index for determining the approximate HLB required for stability of emulsions. In this procedure, a drop of the oil to be emulsified is placed on the surface of aqueous solutions of varying HLB contained in petri dishes. At the highest HLB, complete spreading is observed. As the HLB decreases so does the spreading. The point where the system goes from spreading to non-spreading will be the optimum HLB for most emulsion stability.

Gorman and Hall (8) have observed a quite reasonable correlation between dielectric constant of oil phase and the required HLB number for suitable emulsification.

Emulsion Stability

The particle size or droplet size of the dispersed oil in an emulsion is one of its most important characteristics. It will determine appearance as well as stability. Particles larger than one μ will produce milky white emulsions. Particles between one μ and 0.1 μ will produce blue-white emulsions. Smaller than this size produce from gray semi-transparent emulsions to transparent emulsion.

Particle size is a function of the composition of the ingredients, quantity and type of surface active agent, and the method and forces applied in forming the emulsion. Generally speaking larger quantities of surface active agents produce smaller particle size. Order of mixing also plays an important part. More effective dispersion and smaller particle size usually results when the surface active agent is incorporated in the oil phase prior to mixing with water. The surface active agents will tend to orient themselves at the oil-water interface. The strength and compactness of this interfacial film of surface active agent is important from the standpoint of stability.

The two major examples of instability in emulsions are creaming and breaking. An emulsion is considered to break if it separates into two immiscible phases. These phases may be redispersed upon agitation if the surface active agent is still present. Creaming is not de-emulsification, but rather separation of the emulsion into two emulsions. In one of the two emulsions the concentration of the dispersed phase is higher than in the other. Rate of creaming is usually proportional to the difference in density between the phases.

Some factors which influence the stability of emulsions are:

1. Composition and quantity of emulsifying agent.
2. Presence of electrolytes in the aqueous phase. Large quantities of electrolytes interfere with ease of emulsification and also cause breaking of an emulsion. This becomes significant in seawater.
3. Mode of addition of surface active agent. Thorough mixing of the emulsifying agent with the oil prior to agitation is more likely to produce a stable emulsion.
4. Type and force of agitation. Mixing with high shear tends to break the particles down to smaller size. The greater the shear the smaller the particles and the likelihood of greater emulsion stability.

5. Temperature. At higher temperatures emulsions usually tend to form more readily and break more readily. High temperatures are rarely a factor in oil spill dispersion. However, at extremely low temperatures, oils generally have a very high viscosity and it becomes very difficult to get sufficient agitation to break the mass of oil into tiny droplets. If the oil has become waxlike, it is almost impossible to produce satisfactory emulsion stability.

6. Decomposition of emulsifying agent. Biodegradation or other forms of decomposition will lead to breaking of an emulsion. Hopefully, when this occurs, the oil has become widely dispersed and the biodegradation of the oil is occurring simultaneously with the emulsifying agent.

Item 3 above is very important in the preparation of stable emulsions and it is instructive to discuss the various possibilities in the mode of addition of the components of an emulsion.

1. Emulsifying agent is mixed with water and then oil is stirred into the water. Such a procedure usually results in a coarse unstable emulsion with large oil droplet size.

2. Emulsifying agent is mixed with oil and this mixture is added to water with stirring. This procedure produces an oil in water emulsion which is likely to be stable and uniform. Droplet size may well be in the colloidal range producing good stability.

3. Emulsifying agent is mixed with oil, and water is added to this mixture while stirring. This procedure is likely to produce a very high viscosity water in oil emulsion. Viscosity may become so high that mixing becomes difficult. The stability of this emulsion is good but since it is a water in oil emulsion, it cannot be further dispersed in water without very high power requirements for agitation.

4. Nascent soap is formed in the emulsion leading to good stability. If free fatty acids exist in the oil, and alkali is present in the water, then soap will form as the two phases are mixed together. This in-situ formation of the emulsifying agent (soap) leads to good dispersion.

CHEMICAL COMPOSITION OF OIL SPILL DISPERSANTS

Oil spill dispersants typically contain three types of ingredients.

1. Surface active agent. This is the major active component.

2. Solvents. Solvents may or may not be present for the purpose of diluting the active ingredient, to modify viscosity, adjust freezing point, and to enable more rapid blending or miscibility with oil.

3. Additives. Additional ingredients may be present for the purposes of modifying pH, corrosion inhibition, color and appearance, to increase hard water stability, and as aids in dispersion properties.

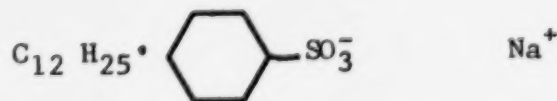
Since the surface active agent is such a vital component of an oil spill dispersant we will examine the chemical composition of these substances at some length.

Surface Active Agents Used in Oil Spill Dispersants

1. Soaps. The oldest and best known of anionic emulsifying agents are the soaps. Soaps are the salts of the long chain fatty acids derived from naturally occurring fats and oils. The fatty acids present in a soap will vary from 8 carbons to 22 carbons in chain length and may possess varying degrees of unsaturation depending on the fat or oil employed. Typical soaps are made by reacting an alkali metal, ammonia or amine with fatty acids derived from coconut oil, rosin and tall oil. Soaps are highly effective emulsifying agents when used in soft water. High concentrations of dissolved salts and electrolytes, particularly heavy metal ions, will precipitate soap. Because of this sensitivity to electrolytes, soaps are not normally the major emulsifying component in oil spill dispersants designed for use in seawater.

2. Sulfonated organics. In this group we include the alkali metal, ammonia or amine salts of sulfonated petroleum oils (petroleum sulfonates or mahogany acids), and the much larger and more commonly used group of alkyl aryl sulfonates.

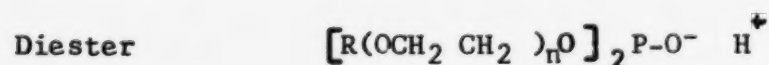
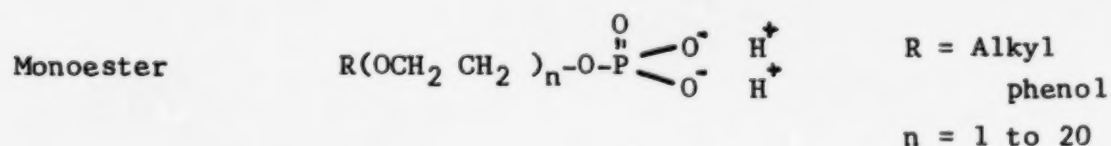
The earlier forms of these compounds were prepared by sulfonation of alkyl benzene with fuming sulfuric acid and later with sulfur trioxide. These compounds are often referred to as ABS. The branched chain alkyl structure of these sulfonates produced very stable molecules incapable of rapid biodegradation (so called hard detergents). In 1965 the detergent industry switched over to the use of straight chain or linear alkyl benzene which produced much more readily biodegradable sulfonates known as LAS. The most widely used of these sulfonates is the linear dodecyl benzene sulfonate.



The formula illustrates the anionic character of the sodium salt of dodecyl benzene sulfonic acid. The sulfonate may be neutralized with any of the alkali metals, ammonia or amines to produce the neutral salt. The amine salts are known to possess greater solubility in oils and are more widely used as emulsifying agents.

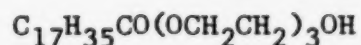
Sulfated organic compounds comprise another large group of surface active agents, but they are not as widely used for oil dispersing. These differ from the sulfonated compounds in that the sulfur atom is linked to the parent molecule through an oxygen atom, whereas the sulfonated sulfur atom is joined to a carbon atom of the parent molecule.

3. Phosphated esters. This group of anionic surface active agents is prepared by reaction of the hydroxy group of a long chain alcohol, alkyl phenol, or linear ethoxylate with phosphorus pentoxide or some other source of the phosphate radical. Conditions of reaction may be controlled to produce varying proportions of mono or di-ester in the end product.

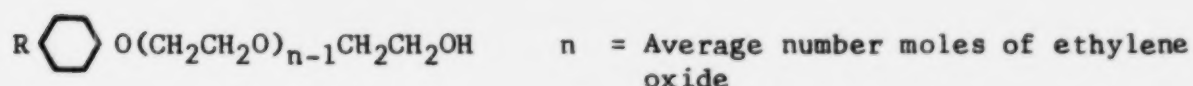


These free acid phosphate esters may be neutralized with alkali metals, amines or ammonia to produce extremely stable compounds with very good tolerance for dissolved salts.

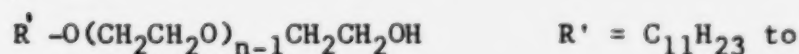
4. Carboxylic Acid Esters of Polyhydroxy Compounds. This large group of nonionic surface active agents are produced by the reaction of fatty acids with polyhydric alcohols or by direct addition of ethylene oxide to the carboxylic hydroxy group. By varying the chain length of the fatty acid as well as the amount of ethylene oxide used in the reaction, the HLB may be controlled. As an example, the monostearic acid ester of triethylene glycol (3 moles of ethylene oxide) is illustrated below.



5. Ethoxylated alkyl phenols and alcohols. This group of nonionic surface active agents is derived by adding ethylene oxide in varying quantities to alkyl phenols or long chain alcohols to produce very stable ether structures. With the trend toward more readily biodegradable surface active agents, straight chain alcohols are more and more replacing the branched chain ethoxylated nonyl and octyl phenols. Eleven to 15 carbon chain alcohols are typically reacted with from 5 to 10 moles of ethylene oxide. Higher ethylene oxide content provides greater hydrophylic character, and lower ethylene oxide content provides greater hydrophobic properties or oil solubility.



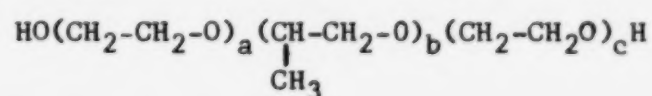
Alkyl phenol ethoxylate APE R = Alkyl-Octyl, nonyl



Linear Alcohol ethoxylate LAE $C_{15}H_{31}$

This series of nonionic adducts exhibits inverse solubility properties in water. The temperature at which an aqueous 1% solution of the compound becomes cloudy when heated is known as the cloud point (23).

6. Block Polymers. These nonionics are typically prepared by adding polyoxyethylene to both ends of a polyoxypropylene chain, with both ends of the resulting molecule termination in hydroxy groups.



By varying the numerical value of a, b and c, a wide variety of molecules may be synthesized to produce the optimum HLB for a particular use.

7. Alkanolamides. These nonionic compounds were first reported by Kritchevsky in 1957 and are often referred to as Kritchevsky condensates (9) (10). Those most widely used in dispersant formulation are

prepared by reacting two moles of diethanolamine with one mole of fatty acid according to the reaction



R = Fatty acid-frequently coconut fatty acid or lauric acid. Commercial products produced by the above reaction will usually be a mixture containing:

Diethanolamine	- 29.0%
Fatty Acid	- 4. %
Ester Amide	- 3.5%
Diethanolamide	- 63.5%

The members of this group of compounds are usually quite viscous and may solidify at room temperature.

Solvents. Since many of the surface active agents applicable to oil spill dispersant compounding are viscous or solid materials, some form of solvent is often necessary in order to reduce viscosity for ease of handling. In addition, the solvent may act to dilute the compound for economic reasons, to depress the freezing point for low temperature usage, to enable more rapid solubility in oil, and to achieve optimum concentration of surface active agent for performance reasons. The presence of a suitable solvent also serves to thin the oil to be dispersed, reducing viscosity and making it more easily emulsifiable.

The three general classes of solvents used in oil spill dispersants are petroleum hydrocarbons, alcohols or other hydroxy compounds, and water.

Petroleum hydrocarbons provide good solvency to aid in penetrating the oil. They reduce viscosity and generally have low freezing points. They are also low in cost. Usually petroleum fractions with boiling points above 300°F are used, and these may produce finished dispersants with flash points as low as 110°F. The proportion of aromaticity is significant, since this effects solubility and emulsification properties as well as toxicity. It is significant that Smith (7) in describing the Torrey Canyon aftermath reports that the aromatic solvents used were 10 times as toxic to marine life as were the surface active agents. Some typical fractions of applicable petroleum solvents include mineral spirits, kerosene, #2 fuel oil, and heavy aromatic naphthas which contain significant quantities of higher alkylated benzenes.

The alcoholic or hydroxy group of solvents include alcohols, glycols and glycol ethers. These solvents also lower the viscosity as well as the freezing points of finished dispersants. In addition, they furnish a co-solvent effect, often needed to mutually dissolve the various ingredients in a dispersant for stability of the compound in storage. This group of solvents may be used in conjunction with petroleum hydrocarbons as well as with aqueous solvent systems. Some of the more frequently encountered chemicals in this group include ethyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol, ethylene glycol mono methyl ether, ethylene glycol mono butyl ether, and diethylene glycol mono methyl ether. The more volatile members of the group are quite flammable.

Water is the least toxic, least hazardous and most economical of the solvents. It does suffer, however, from a lack of solubility or miscibility with oils. Where water is used as the solvent, special problems exist in the choice of surface active agents and other additives in order to provide the necessary miscibility with oils. Glycols and alcohols are used to aid in miscibility as well as freezing point depression when water is used.

Other Additives

Alkalis	- to modify pH
Sodium phosphates	- dispersant aid and water softening
Sodium silicates	- corrosion inhibition and dispersing aid
Ethylenediamine tetraacetic acid	- water softening, heavy metal chelation
Lignin sulfonates	- dispersing aid
Polymerized alkyl naphthalene sulphonates	- dispersant aids
Sodium nitrite	- corrosion inhibitor
Dyestuff	- color identification
Aromatic oils	- covering odor

Because oil spill problems have been spotlighted in the news in recent years, the number of commercially available dispersants has grown rapidly. The imaginative trade names and prices of these compounds sometimes bear little relationship either to efficiency in dispersing oil spills or possible toxic effects. Studies of the available products

indicate that large segments of them can be described through the following classes:

<u>Surface Active Agent</u>	<u>Solvent</u>
Ethoxylated alcohols & alkyl phenols	- Petroleum
Ethoxylated alcohols & alkyl phenols	- Aqueous & Additives
Polyhydric Fatty Acid Esters	- Aqueous & Additives
Alkanolamide	- Aqueous & Additives
Sulfonated Anionics	- Petroleum
Combinations of above	- Aqueous or Petroleum

The aqueous solvent may include such water soluble solvents as alcohols, glycols and glycol ethers.

PRODUCTION AND PROPERTIES OF OIL SPILL DISPERSANTS

The manufacture of oil spill dispersants usually involves a simple blending or compounding operation. The various ingredients may be manufactured elsewhere to dependable reproducible standards. The compounder must exert considerable care in developing the final formulation as well as in developing analytical methods for quality control purposes. The following standardized tests are useful (11):

<u>Test</u>	<u>Method Reference</u>
Color	A.S.T.M. Color D1500-64 Saybolt Color D156-64
pH	A.S.T.M. E-70
Free Alkalinity or free acid	A.S.T.M. D820-58
Total Alkalinity	A.S.T.M. D800-58
Water Content	A.S.T.M. D800-58
Non volatile matter	A.S.T.M. D820-58
Volatile hydrocarbons	A.S.T.M. D800-58 also MIL-C-20207C (12)
Flash point	Cleveland open cup A.S.T.M. D92-66, Pensky-Martens closed tester A.S.T.M. D-93-66 Tag closed tester A.S.T.M. D56-64

<u>Test</u>	<u>Method Reference</u>
Specific gravity	A.S.T.M. D1298-67
Foaming Properties	A.S.T.M. D1173-53
Loss on ignition (Ash)	A.S.T.M. D 800-58
Pour Point	A.S.T.M. D 97-66
Aromaticity of Petroleum Hydrocarbon Solvent	A.S.T.M. D1019, in conjunction with A.S.T.M. D875

The reputable supplier will perform a sufficient number of these tests or others of his own design to confirm the desired composition and performance properties. He will also retain a sample from each batch for periods of six months to two years.

Relationship of Physical Properties to Performance

Viscosity, as stated previously, will effect ease of application. Viscous materials require more powerful pumping equipment. Lower viscosity compounds are likely to penetrate oil faster. The Bureau of Ships Specification MIL-S-22864(13) for oil spill dispersants has established a viscosity maximum of 400 centistokes at 20°F. Such a viscosity insures ease of application, but it could well rule out somewhat more viscous products which may have other advantageous properties.

Flash point information will indicate the flammability hazard associated with the use of a dispersant. The Bureau of Ships Specification MIL-S-22864 has established a 150°F minimum. In view of the fact that oil and fuel spills often represent severe fire hazards, one may well question the advisability of using a dispersant which has a fire hazard of its own.

Composition data will provide information concerning toxicity problems in the handling and use of the dispersant. The presence of highly volatile ingredients may prevent usage in confined areas.

Uniformity and stability of the dispersant in storage is essential, so that stratification or changes in properties do not occur over long periods of time in widely varying storage and temperature conditions.

Dispersants are supplied ready for use or as a concentrate which is diluted with water or petroleum solvent just prior to use. Since oil spills invariably occur without warning, dilution prior to use is often impractical, and the compound is best forwarded to the site of application ready for use.

Biodegradability information concerning the dispersant, as well as the individual surface active agents present in the compound, will be significant in predicting long term contamination caused by the use of the dispersant.

CHEMICAL ANALYSIS OF OIL SPILL DISPERSANTS

Detailed analytic techniques are beyond the scope of this report, but it will be helpful to set down several procedures which will establish the general chemical nature of unknown samples.

Volatile solvents may be determined by a conventional distillation. If the solvents are not water soluble, the steam distillation technique outlined in military specification MIL-C-2027C(12) is useful.

Procedure: "The solvent content shall be determined by weighing 100 + or -0.1 gram of compound into a 1,000 mls. round bottom flask. Add 20 grams of anhydrous barium chloride dissolved in 100 mls. of water to the flask and steam distill the mixture. Collect the distillate in 250 mls. graduated cylinders. Continue the distillation until not more than 1 ml. of solvent comes over with 250 mls. of distillate. Note the total volume of non-aqueous layers. Combine the solvent portions from the several collecting cylinders, dry over anhydrous sodium sulphate, and filter through a #12 fluted Whatman filter paper. Determine the specific gravity at 25°C using a pycnometer; calculate weight % of solvent as follows:

$$\% \text{ solvent} = \frac{\text{vol. non-aqueous steam distillate} \times \text{specific gr.}}{\text{weight of sample}} \times 100$$

The solvent shall be reserved for mixed aniline and chlorinated solvent analysis.

Ash test or loss on ignition will determine the presence of inorganic ingredients.

Analysis for the surface active agent is of most interest (14). Where detailed specific information is required it would be well to start with the method for "Separation of Active Ingredient from Surfactant; Syndet Compositions A.S.T.M. D2358-65T" (11). Once the surfactant has been separated, A.S.T.M. method D-2357-65T may be used for "Qualitative Classification of Surfactants by Infra red Absorption" (11).

In the absence of instruments, qualitative analysis of the surface active agent may be performed as outlined below.

Separation of Surface Active Agent

Dry sample in an oven at 105°C. Reflux sample in 95% isopropyl alcohol for one hour. Filter hot through Whatman #1 filter paper. The filtrate will contain the surface active agent. The residue, if any, will contain inorganic salt such as sodium phosphates or silicates.

Evaporate the filtrate over steam bath and save for qualitative tests.

Ionic activity tests (Weatherburn Test) (15)

- Reagents:
1. Dye solution: 0.03 grams methylene blue, 12 grams concentrated sulfuric acid, 50 grams anhydrous sodium sulphate dissolved in water to make a total of one liter solution.
 2. Anionic surfactant solution-0.05% Aerosol OT (Sodium dioctyl sulfo succinate).
 3. Chloroform

Ionic activity tests (Weatherburn Test) (15)

- Procedure:
1. Into a 25 mls. test tube place 8 mls. of dye solution and 5 mls. chloroform. Add anionic surfactants solution drop by drop, shaking vigorously between drops and allowing phases to separate. Continue adding dropwise until the two layers are equal in color and intensity viewed in reflected light. Usually 10 to 12 drops of anionic solution are required.
 2. Now add 2 mls. of 0.1% solution of the unknown and shake vigorously.

- Results :
1. Chloroform phase (lower) is deeper in color and aqueous phase is mostly colorless — anionic is positive.
 2. Water phase (upper) is deeper in color than the chloroform phase — cationic is positive.
 3. Both phases are more or less the same color — probably a nonionic.
 4. If the aqueous phase has become milky and hence slightly lighter in color, it may still be nonionic. Soaps do not react in this procedure. If both anionics and nonionics are present, the reaction of this test will be anionic positive.

Test for Nonionic (Cationic Negative) (16)

- Reagents :
1. Cobalthiocyanate solution: dissolve 24.0 gms. of potassium thiocyanate (KCNS) and 1.0 gms. of cobalt nitrate ($\text{CoNO}_3 \cdot 6\text{H}_2\text{O}$) in distilled water and dilute to 100 ml. volume.
 2. 0.2 N sulfuric acid: dilute 5.6 mls. of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with distilled water.

- Procedure:
1. To 5 mls. of active ingredient solution add 0.2 N H_2SO_4 dropwise until the pH is about 4 (to indicator paper).
 2. Add 1 ml. of the cobalthiocyanate solution. A blue color is positive for nonionic material providing no cationic material is present.

This test is negative for diethanolamides.

Ignition Test

Ignite about 0.1 grms. of surface active agent on a platinum dish or piece of platinum foil. Heat gently at first and then more

strongly. Note: (1) Ease with which compound burns and decomposes. (2) The odor of gases or vapors evolved, and their acidity or alkalinity to litmus.

Ignite strongly until almost all organic matter has burned off. Cool, add a few drops of 30% hydrogen peroxide, and reheat. If unburned carbon still remains after strong ignition, cool and add several drops of concentrated nitric acid. After standing a few minutes, heat gently until acid has vaporized and then ignite strongly. Repeat the nitric acid addition if necessary until carbon has burned off.

Discussion:

A residue after ignition indicates the presence of a metallic element. If the residue is less than about 1% it is probably contamination and may be disregarded. The metal is likely an alkali metal and may be confirmed by standard procedures.

Alkaline vapors during the ignition indicate the presence of ammonia or amines. Odor of burning sugar indicates glucose, sorbitol or carbohydrate derivatives. Proteins char with a characteristic odor.

Acidic fumes are given off by salts of volatile organic acid and by organic sulphates and sulphonates.

If ash is present, run a standard sodium fusion and use the resulting solution for analytical tests for the presence of sulfur, nitrogen, halogen, phosphorous. If no ash is present, the surface active agent is likely to be nonionic.

If nonionic, and the aqueous solution shows no cloud point on heating, it could be a diethanolamide — nitrogen should be confirmed.

The reader is referred to "Systematic Analysis of Surface Active Agents" by Rosen-Goldsmith (14) for more complete data on analytical procedures.

MEASURING OIL SPILL DISPERSING POWER

Thus far we have discussed physical and chemical procedures which are fairly well documented. Our most vital property — ability to

disperse an oil spill under a wide variety of conditions — is the most difficult property to evaluate. Very little has been published on this subject. The problem is complicated by the large number of variables present under field conditions; to enumerate a few:

- Composition of water
- Composition of oil
- Viscosity of oil
- Temperature of water and air
- Length of time oil has been exposed to atmosphere
- Wind and wave conditions
- Tidal conditions
- Amount of agitation possible
- Method of application of dispersant

In reporting on the Torrey Canyon oil spill, Smith (7) writes that the oil was Kuwait crude oil which contains about 25% volatile ingredients. As evaporation took place the oil became progressively more viscous. It was theorized that after about three weeks at sea, approximately 15% of the original amount would remain as a black tarry asphaltic residue. Evaporation, photo oxidation, as well as bacterial degradation, all contribute to these changes.

The Plymouth Laboratories (7) used an unsophisticated method of determining stability of detergent — oil emulsions. Two mls. of detergent, 2 mls. of Kuwait crude oil, and 96 mls. of sea water were shaken up in a 100 ml. graduate cylinder and allowed to stand. Observations were made of the appearance of the resulting emulsion.

A few emulsion stability tests reported in the literature are worthy of note.

Emulsion Stability of Soluble Cutting Oils. A.S.T.M. D1479-64 (17)

Soluble oil is dispersed at a suitable concentration in an appropriate test water. The emulsion is stored for 24 hours after which the bottom fifth is separated for determination of oil content. Comparing oil concentrations in stored and freshly prepared emulsion gives "the percentage of oil depletion".

In the procedure, 125 mls. quantities of emulsion at various dilutions are stirred in 250 mls. beakers with a four bladed beater at 500 + or -50 rpm for one minute. Emulsion is poured into a 125 mls.

separatory funnel and allowed to stand for 24 hours, after which the bottom 20% is drawn off and transferred to a Babcock milk-test bottle. Sulfuric acid is added to break the emulsion and the bottle is centrifuged 10 minutes or until separation is complete. Stability is calculated in terms of "percentage of oil depletion" at a specified dilution in a given test water.

Emulsion Characteristics of Petroleum Oils and Synthetic Fluids.
A.S.T.M. D1401-67 (17)

This method describes a procedure for measuring the ability of petroleum oils or synthetic fluids to separate from water after an emulsion has been formed. A 40 mls. sample of oil and 40 mls. of distilled water are stirred for 5 minutes at 130°F. in a graduated cylinder. Stirring is done using a 3/4 inch wide by 4 3/4 inch long paddle at 1500 + or -15 rpm. The time required for the separation of the emulsion thus formed is recorded. If complete separation does not occur after 1 hour, the volumes of oil, water, and emulsion remaining at the time are reported.

Emulsion Test from Specification MIL-C-22230 (Ships). (18)

While this test was designed to measure cleaning ability, it is of interest as a basis for developing a laboratory procedure for evaluating oil spill dispersants.

The method calls for preparing a standard soiled metal panel by coating it with Navy Special Fuel Oil. The panel is immersed in jars containing cleaning compound solutions and subjected to agitation on the Fisher oscillating hot plate. The solution is then poured out and allowed to settle for 24 hours. Benzol is poured on the surface and gently stirred to dissolve the supernatant separated oil phase. Using a syringe, a quantity of the benzol-oil solution is removed and the oil content determined photometrically.

Specification MIL-C-22230 also calls for a test of miscibility with sea water. This may well be a legitimate test for screening out dispersants normally used in fresh water which might break down quickly in sea water. In this test one part of compound is mixed with 100 parts of sea water. The solution is heated and agitated for 1 hour and no visible separation of compound should be noted after this period of agitation. For oil spill dispersants the sample should not be heated, but the test run at room temperature.

Sea water as used in MIL-C-22230 is 3 1/2 percent sodium chloride solution. The presence of magnesium and calcium in sea water could be significant in affecting the performance of oil spill dispersants. For laboratory tests it is suggested that the synthetic sea water be prepared according to specification MIL-C-7907A (19).

Sodium Chloride	150.0 grams
Magnesium Chloride, hexahydrate	66.0 grams
Calcium Chloride, dihydrate	9.6 grams
Sodium Sulfate, anhydrous	24.0 grams
Water to make a total of	6 liters

In developing military specification MIL-S-22864 Solvent-Emulsifying, Oil Slick, the Navy has done the most significant work in establishing a performance test for these compounds. This procedure is useable as a basis for developing more general procedures applicable to a wider variety of conditions. Some approaches which bear further investigation are discussed below:

- (a) Simulation of wave action should be explored. Changes in design of the pumping mechanism or possible baffling of the tank may be useful in this connection.
- (b) The test should be conducted using water of the types encountered in the field. Products for use at sea should be tested using synthetic sea water. Products offered for use on inland waterways should be tested using water approximating the composition of these waters. In the Navy tank test initial agitation is obtained by hosing the surface with fresh water. While this is sometimes possible when treating an actual oil spill, it is more likely that agitation will be accomplished using the available water at the site. It is recommended that the entire test be done using the same kind of water so as to more closely approximate field conditions.
- (c) The nature of the oil can have substantial influence on the results obtained in this test. Crude petroleum from different sources varies significantly in content of sulfur, nitrogen, and oxygen. Those crudes containing large proportions of naphthenic and other carboxylic acids, phenols and sulfides would be much more sensitive to alkaline dispersants. The test should be broadened to include a representative group of crude oils as well as other fuels and vegetable oils.
- (d) The Navy tank test utilizes a one to one ratio of dispersant compound to oil. This high ratio of dispersant to oil is unrealistic in

terms of usual field conditions. Those dispersants high in solvent content will tend to lower the viscosity of the oil significantly — to a much larger extent than would be the case if the dispersant were used at more usual proportions of one to five parts oil.

A high specific gravity dispersant which is soluble in the oil would aid the oil in remaining below the surface of the water during the test, even if it were not an effective dispersant.

(e) The method of adding the dispersant, by pouring from a graduated cylinder, needs improvement. The oil tends to spread around on the surface in a very non-uniform manner, and it is up to the operator to try to pour from the cylinder contacting as much of the oil as possible with the dispersant. It would be well to develop some sort of ring device which would tend to confine the oil approximately at its limits of spreadability. The oil spill dispersant may then be gently flowed on or sprayed through a sieve-like device so that it will spread more evenly over the surface. In this way lesser quantities of dispersant may be evaluated. A dwell time, allowing the dispersant to permeate through the oil before agitation, is also significant.

(f) Temperature control is important. Certain of the nonionics are very sensitive to temperature. Oil viscosities vary substantially with temperature. The temperature of the test should approximate typical field conditions, and it would be helpful to develop data which would reflect subfreezing weather conditions.

(g) The condition of any undispersed oil at the conclusion of this test is significant, and should be examined. After the pump is turned off, allow tank to settle for 30 minutes. Now, half submerge the outside of a one liter beaker through the surface at the center of the tank. Hold it stationary in this position for 10 seconds, and then remove it. Using a wash bottle containing the test water, determine whether or not oil clinging to the outside of the beaker is readily rinseable.

Laboratory Determination of Dispersing Potential:

The following procedure is suggested as a basis for development of a laboratory evaluation of dispersants. It is designed to estimate dispersing potential under ideal conditions.

Varying quantities of dispersant are mixed with a constant quantity of oil in order to establish the minimum quantity of dispersant required for effective dispersion.

Weigh out four separate 5 gram portions of oil. Mix thoroughly with 4 gram, 2 gram, 1 gram and 0.5 gram quantities of dispersant respectively.

Pour 500 mls. of specific test water into each of four 1000 mls. beakers. Place a metal panel in each beaker of dimensions approximately 1" by 7" by 1/16". Transfer the treated oil samples to the beakers and agitate on the Fisher oscillating hot plate for one hour.

Let stand one hour. Now carefully remove the metal panel. Holding it vertically reimmerse it in the beaker, keeping it there a few seconds. Now remove it and gently swirl it in a beaker of clean test water. Remove and swirl again in a second beaker of clean test water.

Examine the metal panels for presence of coalesced oil. The minimum concentration of dispersant required to leave a negligible residue of coalesced oil on the panel may be called its dispersing potential.

Other observations may be found useful. For example the aqueous residue may be transferred to a separatory funnel, and dispersed oil content determined after specified periods of standing. The coalesced oil clinging to the walls of the test beakers should be noted — and may be determined photometrically by dissolving in a fixed quantity of benzol.

Multiple tests using synthetic sea water as well as fresh water are suggested. Temperature control may be facilitated through the use of a constant temperature bath placed on the oscillating hot plate.

Field Testing:

The development of a meaningful large scale field test is an extremely complex problem because it is difficult to control the many variables.

Prior experience and discussions with Marine and FWPCA personnel lead to these thoughts:

(a) Comparative tests must be done in similar tidal and climactic environment.

(b) A specific quantity of test oil may be retained within a circular boom.

(c) A weighed quantity of oil spill dispersant may be dispensed using a pressurized fire extinguisher. Alternately, smaller quantities may be dispensed from garden type pressurized sprayers. Special larger units may be constructed to handle specific volumes at specific pressures and with fixed spray nozzles.

(d) Agitation may be accomplished with a fire pumper using carefully controlled pumping pressure, flow rate, and time.

(e) Effectiveness may be determined by sampling within the retaining boom 5 minutes and 30 minutes after agitation. Tidal flow will substantially affect these results.

In this discussion no mention has been made of treatment of oil spills by eduction of the dispersant into a stream of water. While this method is effective for flushing an oil spill from one area to another, it is rarely capable of producing effective dispersion of large quantities of oil. (See the section on Emulsion Stability — mode of addition.) Oily materials which have spread to their ultimate limits and which exist as microscopically thin slicks may be successfully treated with this technique, using the same chemical dispersants.

References

1. Kirk, R. E., Orthmer, D. F. Encyclopedia of Chemical Technology, Inter Science, 1963-1967, 2nd ed.
2. Bennett, H., et al. Practical Emulsions. Chemical Publishing Co., 1968.
3. Becher, P. Emulsions; Theory and Practice. Reinhold, 1965.
4. Amer. Soc. Testing Mats. D 459-64; Definitions Relating to Soaps and Other Detergents.
5. Griffin, W. C., J. Soc. Cosmetic Chemists. 1:311 (1949).
6. Griffin, W. C., J. Soc. Cosmetic Chemists. 5:249 (1954).
7. Smith, J. E., (ed.) Torrey Canyon, Pollution and Marine Life. Cambridge U. Press, 1968.
8. Gorman & Hall, J. Pharmaceut. Sci. 52:442 (1963).
9. Kritchevsky, W., J. Am. Oil Chem. Soc. 34:178 (1957).
10. U. S. Patents 2,089,212 and 2,173,058.
11. Amer. Soc. Testing Mats. Standards. Part 22.
12. Military Specification MIL-C-20207C - Cleaning Compound, Solvent Emulsion, Grease Removing.
13. Military Specification MIL-C-22864A (Ships) - Solvent-Emulsifier, Oil-Slick.
14. Rosen, M. J. and Goldsmith, H. A. Systematic Analysis of Surface Active Agents. Inter Science, 1960.
15. Weatherburn, Can. Text. J. 71(16):45-6 (1954).
16. Amer. Soc. Testing Mats. Committee D-12 files.
17. Amer. Soc. Testing Mats. Standards. Part 17.

18. Military Specification MIL-C-22230 (Ships). Fuel Tank and Bilge Cleaner.
19. Military Specification MIL-C-7907A (WP) - Cleaning Compound, Decontaminating.
20. Fisher Oscillating Hot Plate. Fisher Scientific Co. Catalog. Fairlawn, N. J.
21. International Conference on the Pollution of the Sea by Oil. Proceedings, 1962.
22. Oil Spillage Study; Literature Search and Critical Evaluation for Selection of Promising Techniques to Control and Prevent Damage. Prepared by Pacific Northwest Laboratories (1967). U. S. Dept. of Commerce Clearing House Document AD666289.
23. Standard Methods of Chemical Analysis, Vol. III B, Edited by F. J. Welcher, 6th Edition, 1966, D. Van Nostrand Co., Inc., Princeton, p. 1839.

1	Accession Number W 70-02037	2	Subject Field & Group 05G, 05A, 010	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
5	Organization Federal Water Pollution Control Administration, Northeast Region, Edison, New Jersey, Edison Water Quality Laboratory			
6	Title OIL DISPERSING CHEMICALS, A STUDY OF THE COMPOSITION, PROPERTIES AND USE OF CHEMICALS FOR DISPERSING OIL SPILLS			
10	Author(s) Melvin Z. Poliakoff		16	Project Designation FWPCA Program Number 15080FHS 05/69
			21	Note PB188207
22	Citation FWPCA Water Pollution Control Research Series, ORD-3, May, 1969, 27 p, 23 ref			
23	Descriptors (Starred First) *Dispersion, *Emulsifiers, *Water Pollution control, *Reviews, Chemical analysis, Chemicals, Detergents, Oil, Surfactants, Testing, Emulsions			
25	Identifiers (Starred First) *Oil spillage			
27	Abstract A "state-of-the-art" review is provided for chemicals which are used for dispersing spilled oil. Among the topics discussed are: the history of the development of oil spill dispersants; basic emulsion chemistry, including the nature and properties of surface active agents; chemical composition of oil spill dispersants, including a description of generic chemical types; production of dispersants, properties of dispersants; chemical analysis of oil spill dispersants; and the measurement of oil spill dispersing power.			
Abstractor		Institution		